SILICA REMOVAL WITH SPARINGLY SOLUBLE MAGNESIUM COMPOUNDS. PART I

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ABSTRACT

The main bottleneck in the treatment and reuse of effluents from deinking paper mills that employ reverse osmosis (RO) is the high silica content, which causes membrane fouling that limits the recovery of the treatment. Silica removal with magnesium compounds enables to treat large volumes of water with high removal efficiencies at low cost. Although soluble magnesium compounds are efficient, their use is limited since they increase the conductivity in the treated waters. Therefore the use of sparingly soluble magnesium compounds might be a promising alternative. Three sparingly soluble magnesium compounds (MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$) were studied in this paper at three pHs (10.5, 11.0 and 11.5) and five dosages (250-1500 mg/L) at ambient temperature (~20ºC). Only 40% silica removal was obtained, which is not high enough to work at regular RO recoveries without scaling problems. To increase silica removal, the slurries of sparingly soluble compounds were pre-acidified with concentrated sulphuric acid and tested at the same conditions. In this case, high removal rates were obtained (80-86%) at high pH (11.5), even at ambient temperature. These removal rates would allow working at 75-80% recovery in RO units without scaling problems. This pre-acidification, together with the use of $Ca(OH)_2$ as pH regulator limited the increase of the conductivity of the treated waters to only 0.2 mS/cm. Additionally, the use of $Ca(OH)_2$ instead of NaOH as pH regulator increased the chemical oxygen demand removal from 15% to 25%.

Keywords: silica removal, magnesium, softening, pre-acidification, membrane, fouling, effluent reuse, paper recycling

1.-INTRODUCTION

Paper industry is one of the leading industries in water management and sustainable water use. Although different alternatives have been developed to optimize the use of water in papermaking, there are still some unresolved aspects that limit their implementation at industrial scale. The closure of water loops through the internal reuse of water is limited by the accumulation of contaminants, especially dissolved and colloidal material (DCM), which affects the paper machine runnability and the final product quality [1]. To further reduce water consumption it is therefore necessary to treat and reuse the paper mill effluents. Membrane treatments, such as ultrafiltration (UF) and reverse osmosis (RO) [2, 3], allow to produce the water quality required to reuse the effluent. However, effluents from deinking paper mills are characterized by high silica content, ranging from 50 to 250 mg/L as SiO_2 [2, 4, 5]. This makes the removal of silica a key factor for the reuse of the effluent to work on the RO membrane at recoveries higher than 20% [3] without scaling problems. Membrane fouling caused by silica is a bottleneck as silica scaling in RO membranes is severe and, once it is formed, it is very difficult to remove by chemical cleaning [6, 7]. This scaling causes decline in water production rates, low permeate quality, unsteady-state operation conditions, higher energy consumption and serious damages in the membranes that shorten their lifetime, limiting the technical and economic feasibility of the whole treatment chain [8, 9]. Furthermore, the environmental legislationsets stringent limits to the level of silica allowed in the effluents: 50 mg/L in Finland, Canada and United States [5]. Therefore, there is a need to develop cost effective technologies to treat large volumes of high silica content industrial waters.

In papermaking, silica cannot be reduced at its source since sodium silicate, is necessary to: (i) stabilize the hydrogen peroxide for bleaching; (ii) take advantage of its buffering and saponification properties; (iii) assist ink particles dispersion and influence their size; (iv) collect ink; (v) reduce fibre losses; and (vi) avoid the flotation of fibres [10, 11]. Several attempts have been made to reduce its use [12, 13]; however, due to its great variety of functions and low cost, its substitution is still very difficult in deinking papermaking operations.

Silica can be found in crystalline and amorphous forms. There are various forms of crystalline silica, but the most abundant one is quartz, having a very low solubility in water, around 6 mg/L (as SiO_2) at 25ºC. On the other hand, amorphous silica has a solubility of 100-140 mg/L (as SiO_2) at 25ºC [14, 15]. Moreover, amorphous silica can be classified as dissolved, colloidal and particulate silica. Dissolved silica includes polysilicic acid and oligomeric species such as dimers, trimers or oligomers. Colloidal silica stands for more highly polymerized species. Particulate silica is larger than the colloidal one [16]. Both soluble and colloidal silica cause scaling problems on reverse osmosis membranes [7]. When the concentration of soluble silica exceeds its solubility, it precipitates on the membrane surface alone or with other products. In the case of colloidal silica, fouling occurs due to the accumulation of the colloids formed in the bulk solution, and accumulates on the membrane surface [16, 17].

Although there are many silica removal techniques proposed in the literature [18], it is usually carried out during softening processes or by coagulation at high pH [2, 4, 5, 19, 20].

Coagulation with aluminum-based salts is very effective at ambient temperature, but high dosages (2500-5000 mg/L) are required to achieve high removal rates and the use of hybrid coagulants which increases considerably the treatment cost [4]. On the other hand, when silica removal is carried out during softening, it is necessary to ensure that enough hardness is present in the water. Thus, the addition of magnesium compounds is a preferred option, since higher silica removal is achieved with a higher Mg/Ca ratio at constant total hardness [21].

Previous studies have shown that 80-90% silica removal can be achieved adding $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ at high pH (11.5) with dosages of 1500 mg/L at ambient temperature. This high pH level needed was directly translated into an important increase in the conductivity of the waters, which could make necessary the post-treatment of the RO rejects and may compromise the economic feasibility of the whole effluent reuse treatment. However, this problem could be partially solved with the use of $Ca(OH)_2$ as pH regulator [22]. Another approach would be reducing the total dissolved solid concentration (TDS) by using sparingly soluble magnesium compounds instead of soluble magnesium as tested in previous studies [22].

Part I of this study aims to gain new knowledge in the use of sparingly soluble compounds to treat high silica content industrial effluents at ambient temperature. The treatments with MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$) were optimized in terms of dosage, pH and type of pH regulator. Additionally, the possibility of increasing silica removal rates through pre-acidification of the slurries was studied. The objective was to achieve the silica removal necessary (80-90%) to increase RO recovery from 20% to 60-80%, in order to make the effluent reuse process technically and economically feasible. Part II focuses on equilibrium and kinetic studies at different temperatures of the most efficient sparingly soluble magnesium compound (MgO) and the main silica removal mechanisms.

2.-MATERIALS AND METHODS

2.1.-Water Samples

This study was carried out with the effluent of a Spanish paper mill that uses 100% recovered paper to produce newsprint. The mill has an integrated wastewater treatment plant consisting of a primary treatment by dissolved air flotation and a secondary treatment based on an aerobic digestion of the waters on a moving bed biofilm reactor, followed by a secondary dissolved air flotation. Water samples from the final effluent were taken before its discharge to an urban wastewater treatment plant. Samples were stored at 4 ºC during the tests and no sets of trials longer than five days were carried out. Table 1 summarizes the main characteristics of the effluent considered.

Table 1.- Characteristics of the paper mill effluent.

RAW WATER	
pH	8.3
Conductivity (mS/cm)	2.20
Cationic Demand (meq/L)	0.74
Total Solids (mg/L)	1990
Total Suspended Solids (mg/L)	83
COD (mg/L)	430
BOD_5 (mg/L)	150
Turbidity (NTU)	141
Total Alkalinity (mg/L $CaCO_3$)	735
DISSOLVED FRACTION	
Total Solids	1890
Turbidity (NTU)	6.5
Silica (mg/L SiO_2)	190
COD (mg/L)	355
Sulphates (mg/L)	237
Chlorides (mg/L)	126
Calcium (mg/L)	26.5
Magnesium (mg/L)	2.7

2.2.-Chemicals

Three sparingly soluble magnesium compounds of analytical grade, MgO (solubility 0.086 g/L, 20ºC), $Mg(OH)_2$ (solubility 0.012 g/L, 20ºC) and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ (solubility 0.0375 g/L, 20ºC) were studied. Slurries of 10 w/v % were prepared with distilled water on a daily basis. When necessary, pre-acidification of the slurries was carried out with H_2SO_4 (96%). Two different pH regulators were used to increase the pH to the desired values: NaOH and $Ca(OH)_2$, both of analytical grade and also prepared 10 w/v % in distilled water on a daily basis. All products were supplied by PANREAC (Barcelona, Spain).

2.3.-Methodology for jar-tests

For each magnesium compound, 6 dosages were tested (from 250 to 1500 mg/L) at 3 different pHs: 10.5, 11.0 and 11.5. These pHs were selected according to previous studies with the same type of water [22]. Magnesium compounds were tested using NaOH as pH regulator. Once the most efficient compound was selected, pH regulator was varied, comparing the efficiency of NaOH and $Ca(OH)_2$.

First, the pH of the samples was adjusted by adding NaOH (10 wt.%) to 250 ml of sample. After 1 min of mixing at 200 rpm, the magnesium compound being tested was added and mixed for a period of 15 min at 200 rpm, according to previous studies [22], and then, the waters were allowed to settle for 1 h. Finally, the clarified waters and the dissolved fraction, obtained by centrifugation at 2000 g during 15 min in a Hettich Zentrifugen Universal 16, were characterized. All trials were carried out at room temperature (20ºC ±2 ºC) by duplicate. The average error between replicates was always under 5%.

The optimization of the pH regulator was carried out following the same jar-test methodology, using the most efficient magnesium compound according to results obtained, i.e. pre-acidified MgO. Three different dosages (500, 1000 and 1500 mg/L) were tested with the two pH regulators at three pHs (10.5, 11.0 and 11.5).

Mixing was carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. The pH was measured using a model GLP 22 (Crison, S.A), according to Standard Method 4500 [23], and the conductivity was measured with a model GLP 31 (Crison, S.A.), according to the ISO 7888. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as mg/L of SiO_2. Chemical oxygen demand (COD) was measured according to the Standard Method 5220-D [23]. Alkalinity was measured by titration with sulphuric acid 0.1N using a pH electrode connected to an automatic titrator Compact I (Crison Instruments S.A.) to reach pH 4.5, according to EPA 310.1 (1983) method. Sulphate content was measured using Nanocolor® sulphates method (Macherey-Nagel GmbH). Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986 in a SpectraAA 220

spectrophotometer supplied by Varian. Turbidity was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027. Finally, an image analysis of the precipitate particles was carried out in a Jeol JSM-6400 Scanning Electron Microscope (SEM). This SEM is configured with an energy dispersive X-ray analyzer (EDS system) which enables the SEM to perform elemental analysis of the solid.

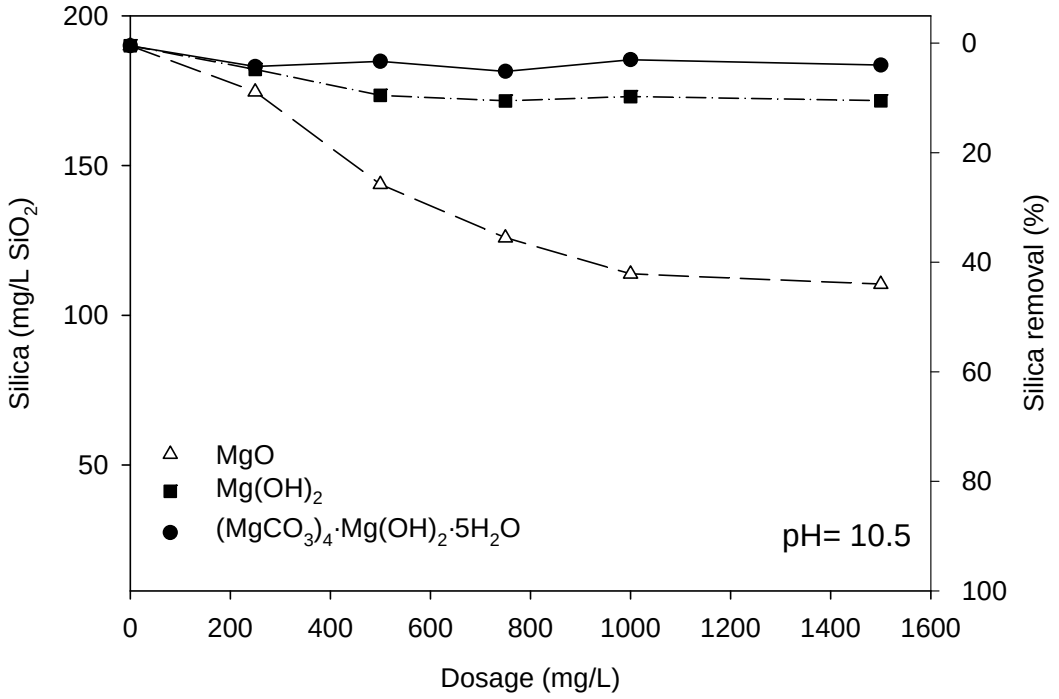
3. RESULTS AND DISCUSSION

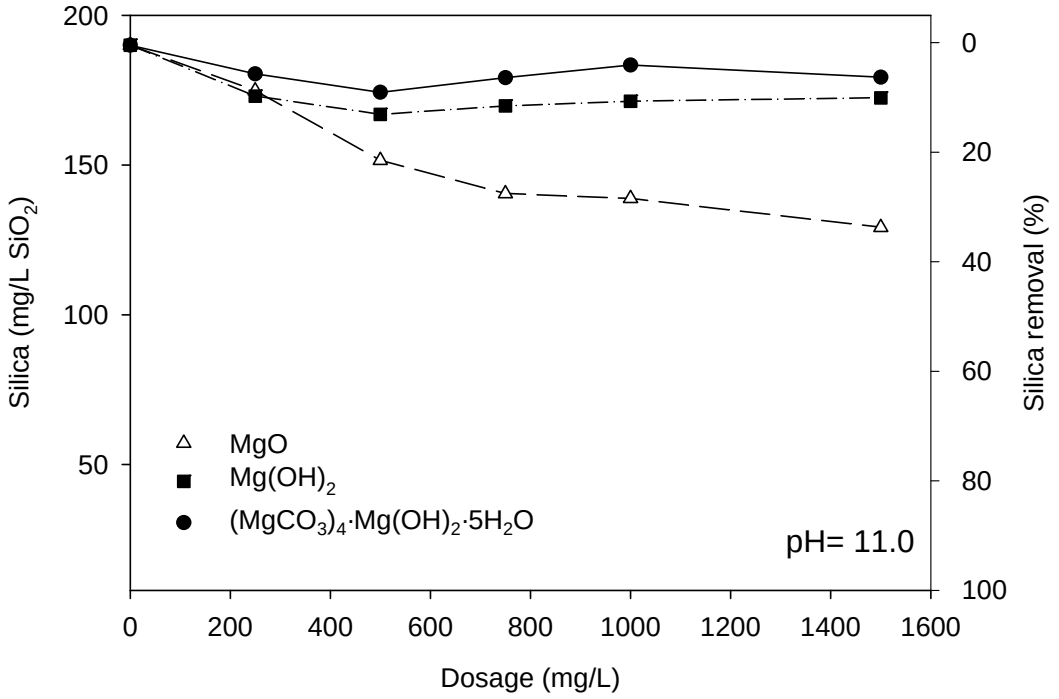
3.1. Silica removal with sparingly soluble magnesium compounds

Figure 1 shows silica removal rates obtained with different dosages of MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ at three initial pHs (10.5, 11.0 and 11.5). MgO was the most effective product, achieving silica removal rates of 40% at pH 10.5 and dosages over 1000 mg/L. With this product, silica removal decreased when increasing the initial pH. Maximum removal rates, obtained at pH 11.0 and 11.5 with 1500 mg/L of MgO, were 32% and 12%, respectively. On the other hand, silica removal rates achieved with $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ were lower than 20% and 10%, respectively, for all the dosages at the three pHs tested. With these two products, silica removal only slightly increased along with the pH and dosage. $Mg(OH)_2$ showed similar removal rates at pH 10.5 and 11.0 and slightly higher removals at pH=11.5. The variations in silica removal rates with $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ were very small and within the experimental error for all the pHs and dosages tested.

The low removal rates obtained with the three products could be attributed to the low solubility of these magnesium compounds and, consequently, the low concentration of dissolved magnesium that is available to react and precipitate either as fresh $Mg(OH)_2$ or magnesium silicates of different stoichiometries [22]. The higher efficiency in silica removal by MgO can be explained through its higher solubility (0.086 g/L) and its higher magnesium content of 60.3 wt.%. This is translated into around 52 mg/l of dissolved magnesium at equilibrium. Using MgO, silica removal increased with the dosage and decreased with pH because MgO solubility decreases at higher pH. The final Mg contents in the water was around 12 mg/L at pH=10.5, 4 mg/L at pH=11.0 and 2.5 mg/L at pH=11.5. Although silica removal increases with pH, the solubility of the

sparingly soluble compounds decreases. In this sense, magnesium concentration in the treated water remained constant, which could indicate that magnesium is being consumed to co-precipitate with silica and the dissolution equilibrium moves towards the dissolution of more magnesium oxide. With $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, the final dissolved magnesium in the water did not vary with the dosage and pH, remaining constant at 12.5 mg/L and 2.5 mg/L, respectively. Although working at lower initial pHs would increase the amount of dissolved magnesium, silica solubility decreases at lower pHs and thus silica removal.


Silica (mg/L SiO2)
Silica removal (%)
Dosage (mg/L)
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pH= 10.5


Silica (mg/L SiO2)
Silica removal (%)
Dosage (mg/L)
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pH= 11.0

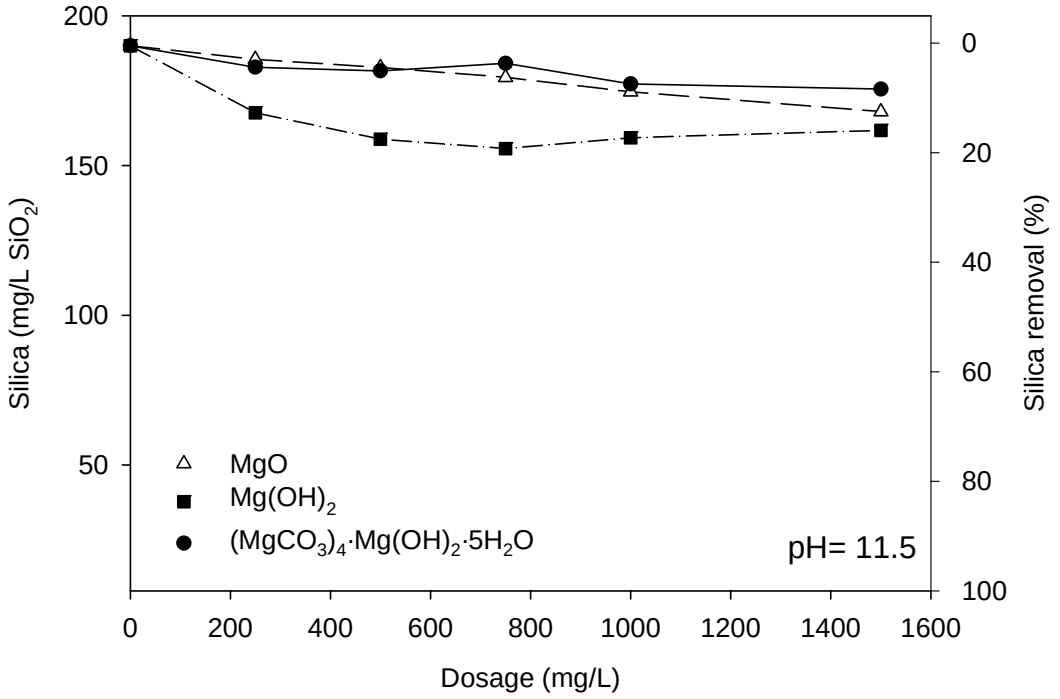


Figure 1- Silica removal vs. dosage at different initial pH with MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$.

COD is another important parameter to take into account as it contributes to the organic fouling of the membrane. As shown in figure 2, the maximum COD removals were around 15% with all the products. These removal rates were similar to the ones obtained with soluble magnesium salts ($MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$) at similar conditions as reported in a previous study [22]. Although significant, this decrease in COD values may not have a significant impact on the organic fouling in subsequent membrane treatments.

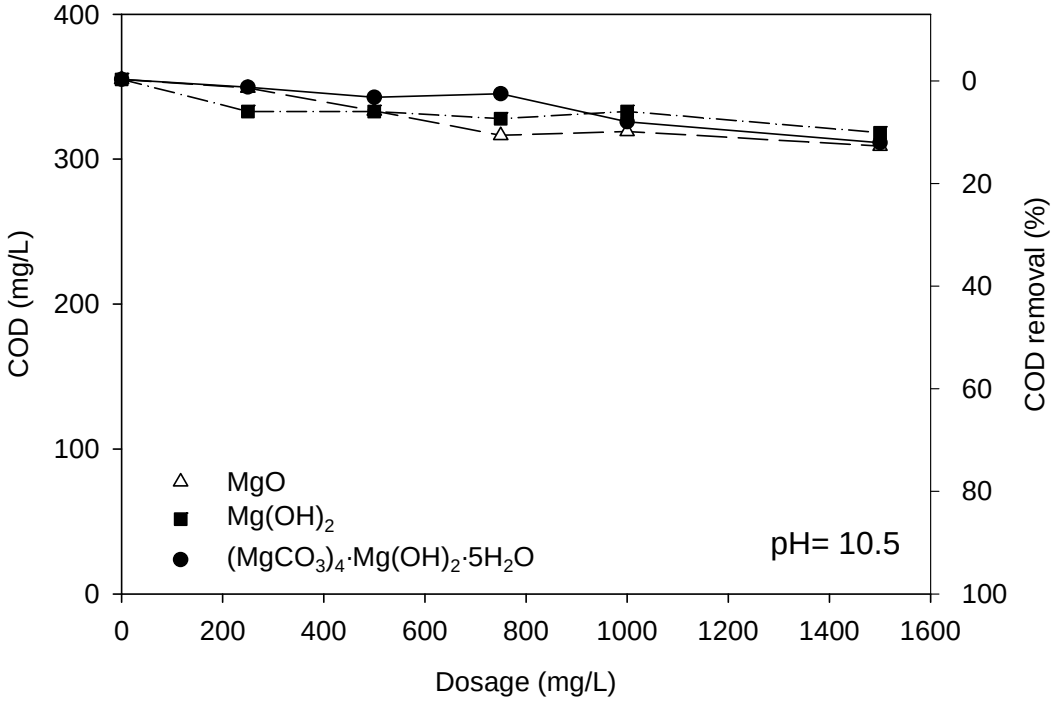
Soluble magnesium salts can achieve high silica removal rates working at high pHs, however, the high final conductivity of the treated waters is a limitation. In the particular case of the paper mill studied, the conductivity of the final effluent cannot exceed 7.5 mS/cm for its direct discharge to the sewage system without any post-treatment. The increase of conductivity in the treated water is mainly caused by the initial pH adjustment and, to a lower extent, by the magnesium compound dosage. In this sense, the use of sparingly soluble magnesium compounds has the advantage of not increasing the conductivity due to their low solubility. The conductivity increase caused

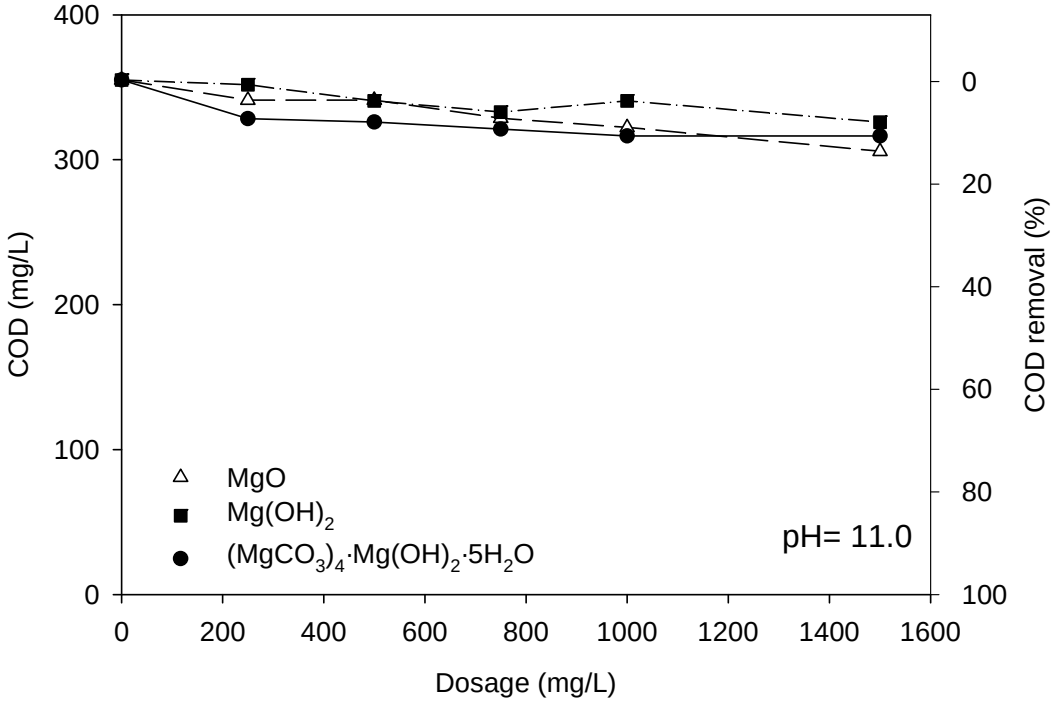
by the pH regulation was 0.8, 1.0 and 1.5 mS/cm at the initial pH values of 10.5, 11.0 and 11.5, respectively. On the other hand, the increase in conductivity induced by the three magnesium compounds tested was around 0.1-0.2 mS/cm at the three pH levels, regardless the dosage used. Thus the final conductivities with the three magnesium compounds were around 2.9, 3.3 and 3.6 mS/cm at pH=10.5, 11.0 and 11.5, respectively.

Monitoring the final alkalinity and pH of the water allows studying the silica removal process, as the precipitation of $Mg(OH)_2$ and/or silicates consumes alkalinity and so the final pH of the water is lower. With the sparingly soluble magnesium compounds, the final pH and alkalinity remained almost constant. The pH variation with the 3 products at the 3 pHs and with the maximum dosage was always smaller than ± 0.1 pH units with the exception of $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ at pH= 11.5 (± 0.3 pH units). This was due to the fact that the low silica removal rates achieved and the hydroxide groups consumed were re-established through the dissolution of the magnesium compounds to maintain the equilibrium.

Regarding turbidity, it increased with the magnesium compound dosage, due to the higher concentration of the sparingly soluble magnesium compound in the treated water, and there were small variations with pH and the magnesium compound used. The turbidity of the clarified waters ranged from 60 to 300 NTU, depending on the treatment, and dissolved turbidity varied from 6 to 9 NTU.

The low solubility of magnesium compounds used resulted in a low concentration of dissolved magnesium and, consequently, in small silica removal rates. Different strategies could be used to increase silica removal, e.g. to increase the working temperature to kinetically favour the dissolution of the magnesium compounds, to increase the contact time or to increase the dissolved magnesium by pre-acidifying the magnesium compound slurries before use. A controlled pre-acidification of the slurries was selected as it is a cheap option to increase dissolved magnesium and could increase the final water conductivity in a lesser extent than soluble magnesium compounds when treating waters at ambient temperature.


COD (mg/L)
COD removal (%)
Dosage (mg/L)
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pH= 10.5


COD (mg/L)
COD removal (%)
Dosage (mg/L)
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pH= 11.0

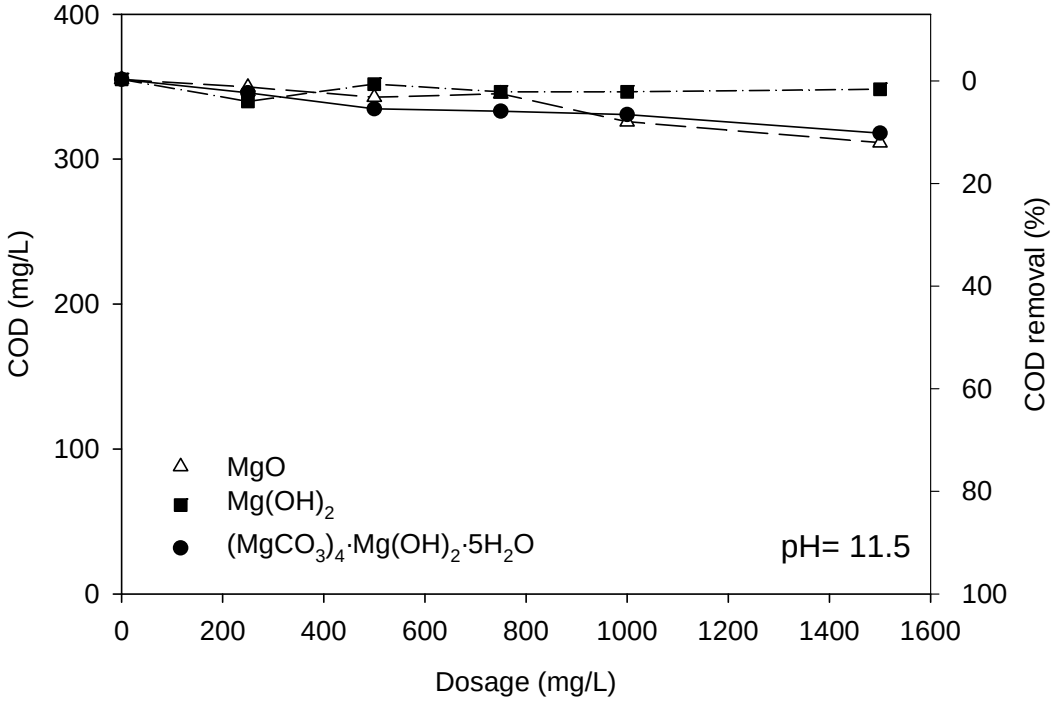


Figure 2- COD removal vs. dosage at different initial pH with MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$.

3.2. Silica removal with pre-acidified magnesium compounds

3.2.1- Characteristics of pre-acidified slurries

Three levels of acidification were tested for the 10 w/v% slurries of each sparingly soluble salt: 9.8, 19.6 and 57.6 g of H_2SO_4/L of slurry. Table 2 summarizes the main characteristics of the slurries with and without pre-acidification. Dissolved magnesium was measured after 30, 60 and 90 min in each slurry at the three acidification levels and only variations in dissolved magnesium below 1% were observed for all the products, indicating the stability of these products. The highest pre-acidification level (57.6 g of H_2SO_4/L of slurry), was selected to carry out further studies as it was the one allowing enough dissolved magnesium for a possible complete silica removal for the three sparingly soluble salts. Although higher levels of pre-acidification could be even more efficient, they would increase the conductivity and sulphates concentration in the slurries, and this is exactly what we tried to avoid using sparingly soluble compounds compared to soluble salts such as $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$.

Table 2.- Characteristics of the slurries with and without pre-acidification.

Magnesium compound	pH	Conductivity (mS/cm)	Dissolved magnesium (g/L)	SO_4^{2-} (g/L)
MgO	11.5	0.2	4.9	0.0
p.a. MgO	9.8	20.4	18.9	54.2
$Mg(OH)_2$	10.3	0.5	5.6	0.0
p.a. $Mg(OH)_2$	9.5	31.3	19.4	54.0
$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$	9.9	0.4	0.87	0.0
p.a.$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$	8.3	25.6	15.2	54.3

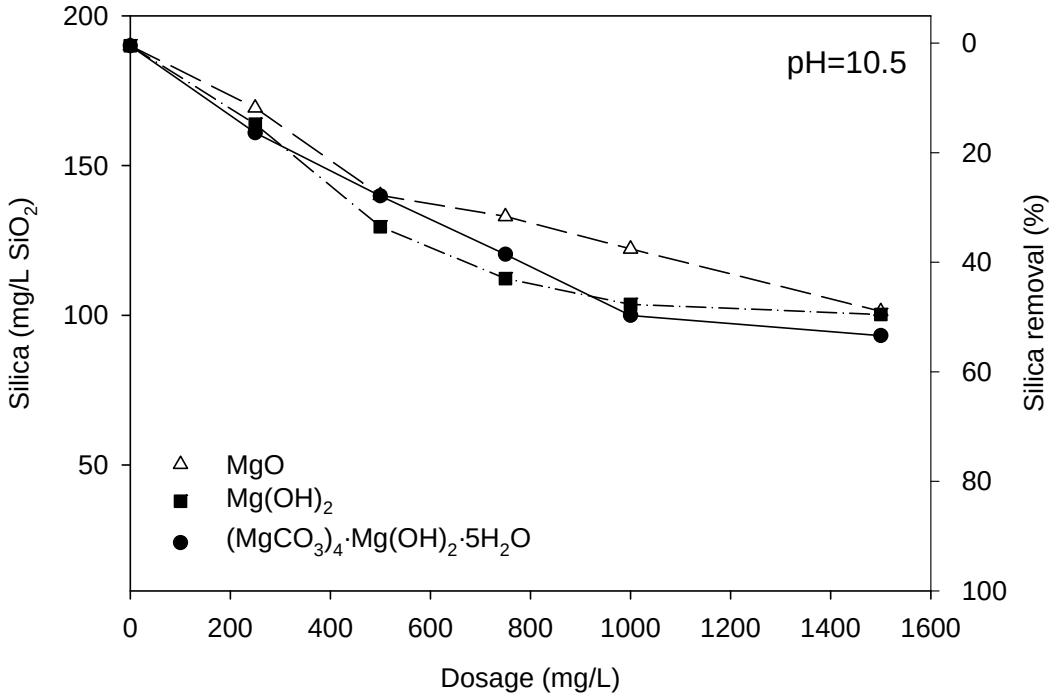
* p.a. means pre-acidified slurry.

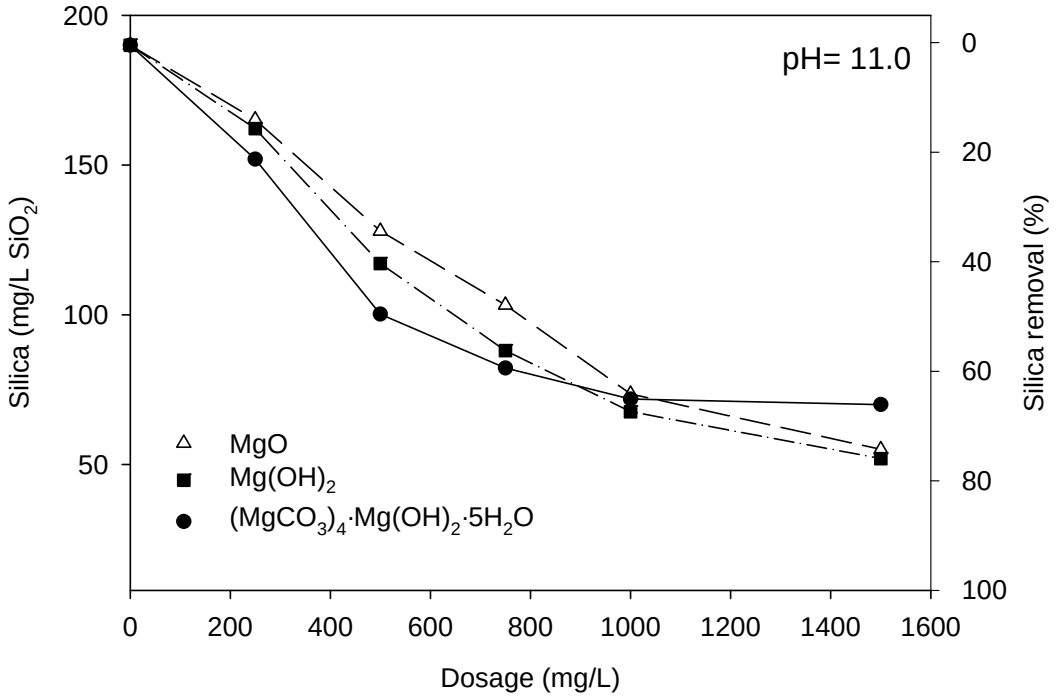
3.2.2- Silica removal with pre-acidified slurries

Silica removal was significantly increased using the slurries pre-acidified with 57.6 g of H_2SO_4/L of slurry. As shown in figure 3, maximum removal rates were obtained at the highest pH (11.5) and dosage (1500 mg/L), being 86% silica removal for both MgO and $Mg(OH)_2$ and around 80% silica removal for $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$.

Silica removal increased with pH and dosage, as there are more hydroxide groups, dissolved silica and dissolved magnesium available to precipitate as magnesium silicates or $Mg(OH)_2$ where silica is adsorbed/entrapped. At the lowest magnesium compound dosage, the increase in silica removal with the increasing initial pH was lower than at the higher dosages. For example, with 250 mg/L of MgO, silica removal was 11, 13 and 17% at pH=10.5, 11.0 and 11.5, respectively. On the other hand, with 1500 mg/L of MgO, silica removal increased from 47% at pH=10.5 to 76% at pH=11.0 and 86% at pH=11.5 with the same product. This indicates that at low dosages, the level of dissolved magnesium is the limiting factor, while in conditions of abundance of the magnesium compound pH (i.e. the availability of hydroxide groups) is the limiting factor. At pH=10.5, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ were more efficient than MgO, which was opposite to their behavior at pH=10.5 without pre-acidification (figure

1a) where MgO was the most efficient product. Silica removal rates obtained with 1500 mg/L of pre-acidified $Mg(OH)_2$ were 47, 73 and 86% at pH=10.5, 11.0 and 11.5, respectively. Finally, with 1500 mg/L of pre-acidified $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, silica removal rates were 51% at pH= 10.5, 63% at pH=11.0 and 70% at pH=11.5. Comparing these silica removal values with the ones obtained without pre-acidification, 70% improvement was obtained at the optimum conditions (pH=11.5 and 1500 mg/L dosage), indicating that pre-acidification of sparingly soluble salts allows obtaining high silica removal efficiencies even at ambient temperature.


pH=10.5
Silica (mg/L SiO_2)
Silica removal (%)
Dosage (mg/L)
MgO
$Mg(OH)_2$
$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$
200
150
100
50
0
20
40
60
80
100
0
200
400
600
800
1000
1200
1400
1600


pH= 11.0
Silica (mg/L SiO_2)
Silica removal (%)
Dosage (mg/L)
MgO
$Mg(OH)_2$
$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$
200
150
100
50
0
20
40
60
80
100
0
200
400
600
800
1000
1200
1400
1600

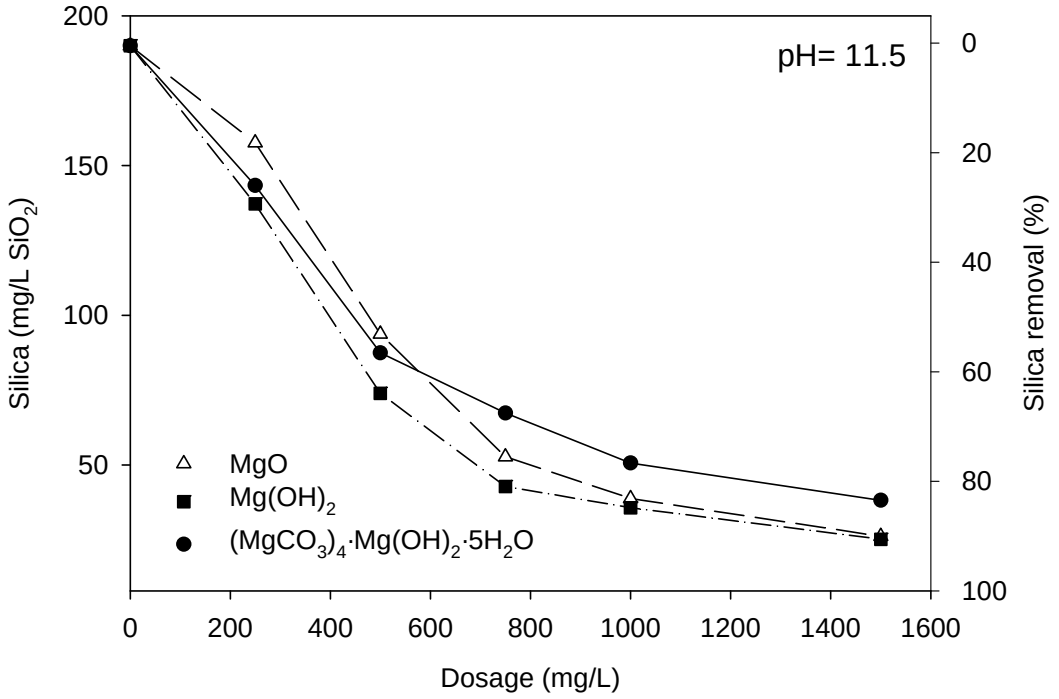


Figure 3- Silica removal vs. dosage at different initial pH using pre-acidified MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$.

The maximum silica removal rates obtained after pre-acidification were similar to the ones obtained in previous studies [22] using soluble magnesium compounds with a similar effluent having approximately the same silica contents. In this case, silica removal rates of 90% and 77% were obtained with $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ with a similar magnesium compound requirement (table 3). Although pre-acidified salts required also 4.7 mg/L H_2SO_4 per mg/L of silica removed, this addition would not increase significantly the cost of the treatment as H_2SO_4 as it is a cheap product (46 €/t) [24]. Additionally, MgO, $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ have similar prices (250-350 €/t) [24], which makes the use of pre-acidified MgO competitive it terms of costs compared to soluble magnesium salts. Moreover, the price of $Mg(OH)_2$ (750 €/t) is approximately twice as expensive than the other magnesium compounds while its use would not further improve silica removal.

The results obtained with pre-acidified magnesium compounds were also competitive with others reported in the literature (table 3). Negaresh et al. [2], for example, achieved 90% silica removal with higher magnesium compound requirements while Zeng et al.

[20] obtained 67% silica removal using a similar amount of magnesium compound but also adding a zinc coagulant.

Table 3. Magnesium requirements for silica removal.

References	**Initial SiO_2 (**mg/L)	**Silica removal** (%)	**pH or NaOH** (mg/L) /(mg/L SiO_2 removed)	**Treatment** (mg/L) /(mg/L SiO_2 removed)
Present study	190	86	pH= 11.5	MgO: 9.1 H_2SO_4: 4.7
		86	pH= 11.5	$Mg(OH)_2$: 9.1 H_2SO_4: 4.7
		80	pH= 11.5	$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$): 9.8 H_2SO_4: 4.7
Latour et al.[22]	180	90	pH= 11.5	$MgCl_2 \cdot 6H_2O$: 9.2
		77	pH= 11.5	$MgSO_4 \cdot 7H_2O$: 10.6
Negaresh et al.[2]	120	90	pH= 10.9	$MgSO_4 \cdot 7H_2O$: 23.3
Zeng et al. [20]	140	67	NaOH: 6.7	$MgCl_2 \cdot 6H_2O$: 8.9 $ZnSO_4 \cdot 7H_2O$: 1.7

The analysis of the solids formed by SEM-EDX (figure 4), also confirmed by other studies in the literature [22, 25], indicates that Si/Mg ratio in these solids varied between 0.5 and 1 (table 4), which is in agreement with the formation of a mixture of forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$). Without pre-acidification, the magnesium contents in the water was the limiting factor for silica removal; however, according to the precipitates formed and the level of dissolved magnesium in the acidified slurries, the magnesium concentration dissolved after pre-acidification was not the limiting factor for any of the products to achieve high silica removal. Therefore, similar silica removals were obtained for all the magnesium compounds used.

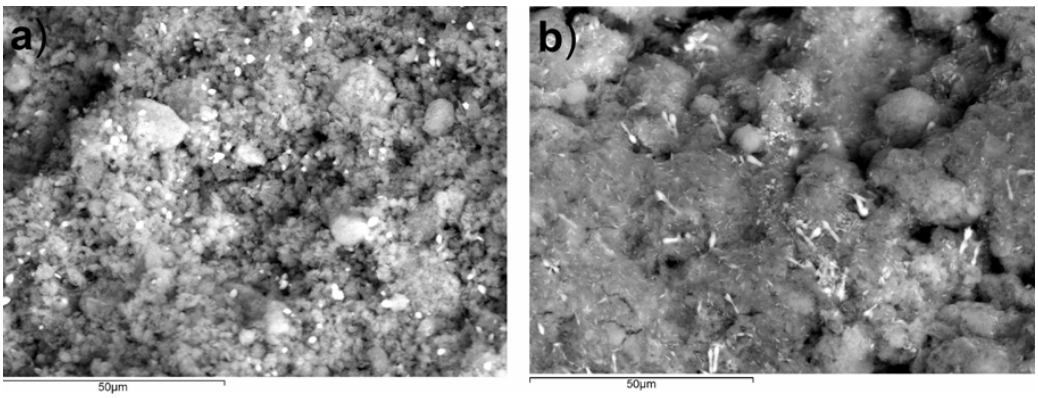


Figure 4. SEM-EDX images of the typical solids obtained after the treatment

Table 4. Composition of the of the solids obtained after precipitation

Solid	O (wt.%)	Mg (wt.%)	Si (wt.%)	P (wt.%)	Ca (wt.%)	Si/Mg (molar)
a)	46.6	28.3	24.2	1.0	7.9	1.03
b)	48.7	30.5	16.5	1.0	3.4	0.47

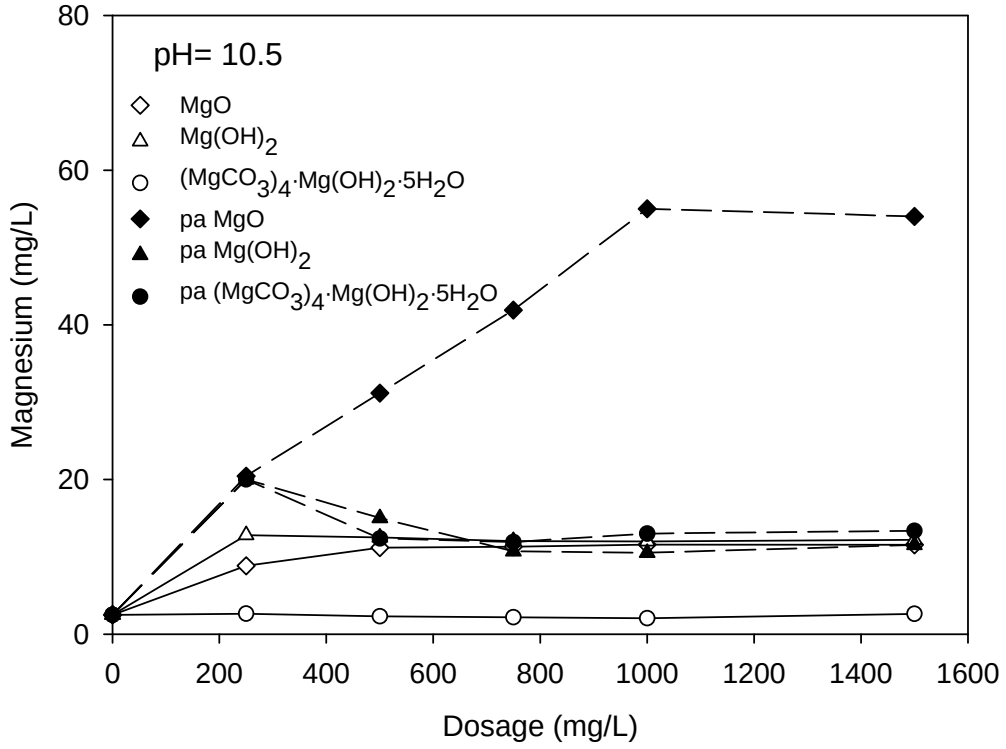
Figure 5 shows the final magnesium concentration in the treated water with and without pre-acidification of the magnesium compounds. With the non-pre-acidified slurries magnesium concentration depends on the solubility of the sparingly soluble salts at each operational pH and on the magnesium content in the molecule. Thus MgO and $Mg(OH)_2$, according to their magnesium contents (60.3% and 41.7% respectively), showed higher final magnesium concentrations than $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ (25.0% Mg content). On the other hand, final Mg concentration with MgO decreased with the operational pH and, in the case of $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, magnesium solubility remained constant.

Pre-acidified MgO was the product resulting in the highest magnesium concentration in the treated water, it varied between 54-70 mg/L at the maximum dosage. In the case of $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, at the maximum dosage and at the three pHs tested, magnesium in the treated water was lower around 15 mg/l.

The final magnesium concentration in the water is higher with pre-acidified MgO than with the other two magnesium compounds due to the higher equilibrium concentration of magnesium at the operational pH. Although the levels of dissolved magnesium in the slurries were similar for MgO and $Mg(OH)_2$ (table 2), both slightly higher than for $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, after precipitation of magnesium silicates, the levels of dissolved magnesium were mainly governed by the solubility equilibrium of these compounds, as the operational pH was much higher than the pH of the pre-acidified slurries. According to the solubility of magnesium in water at 20ºC, its concentration in water would be around 52 mg/L for MgO, 5 mg/L for $Mg(OH)_2$ and 9.4 mg/L for $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$. These values are very close to the ones observed in the treated water with small differences between the theoretical conditions (pure water and

20 ºC) and the real ones. The fact that the final magnesium concentration with $Mg(OH)_2$ was higher than with $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ was due to the operational pH, which was more similar to the pH of the slurry in the case of $Mg(OH)_2$ than in the case of $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$.

Considering that silica solubility is around 120-140 mg/L, maximum silica removal of 86% obtained with both MgO and $Mg(OH)_2$ would allow working at 75-80% recoveries in the RO membranes without silica scaling problems. In the case of using $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, it would be possible to work in the range of 70-75% recoveries as a lower maximum silica removal rate was obtained (80%). However, it would also be possible to work at intermediate recoveries (60-65%) under softer conditions away from the optimum (pH=11.5 and 1500 mg/L dosage). For example, selecting pH=11.0 to work with 1500 mg/L of MgO or $Mg(OH)_2$ would reduce significantly the treatment cost and the conductivity of the waters treated. Another possibility would be working at pH=11.5, but at lower dosages like 750-1000 mg/L of MgO or $Mg(OH)_2$, or even with 1000 mg/L of $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, which also reduces the costs, but not much the conductivity of the water treated.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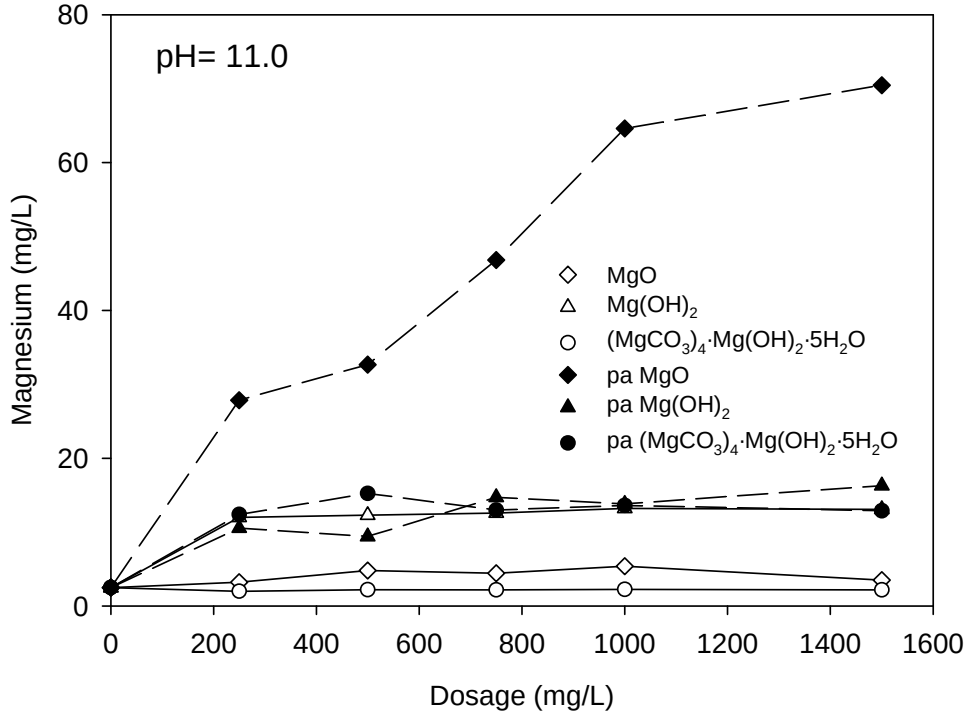
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pa MgO
pa Mg(OH)2
pa (MgCO3)4·Mg(OH)2·5H2O
Magnesium (mg/L)
Dosage (mg/L)
0
20
40
60
80
0
200
400
600
800
1000
1200
1400
1600


pH= 11.0
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pa MgO
pa Mg(OH)2
pa (MgCO3)4·Mg(OH)2·5H2O
Magnesium (mg/L)
Dosage (mg/L)
0
20
40
60
80
0
200
400
600
800
1000
1200
1400
1600

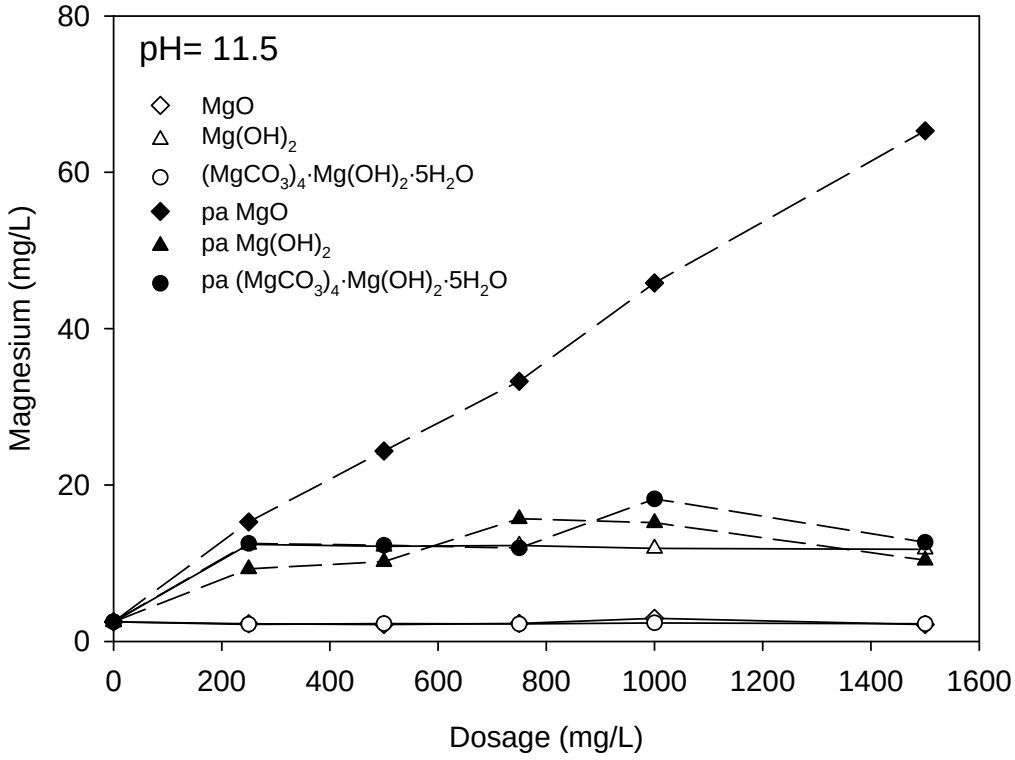


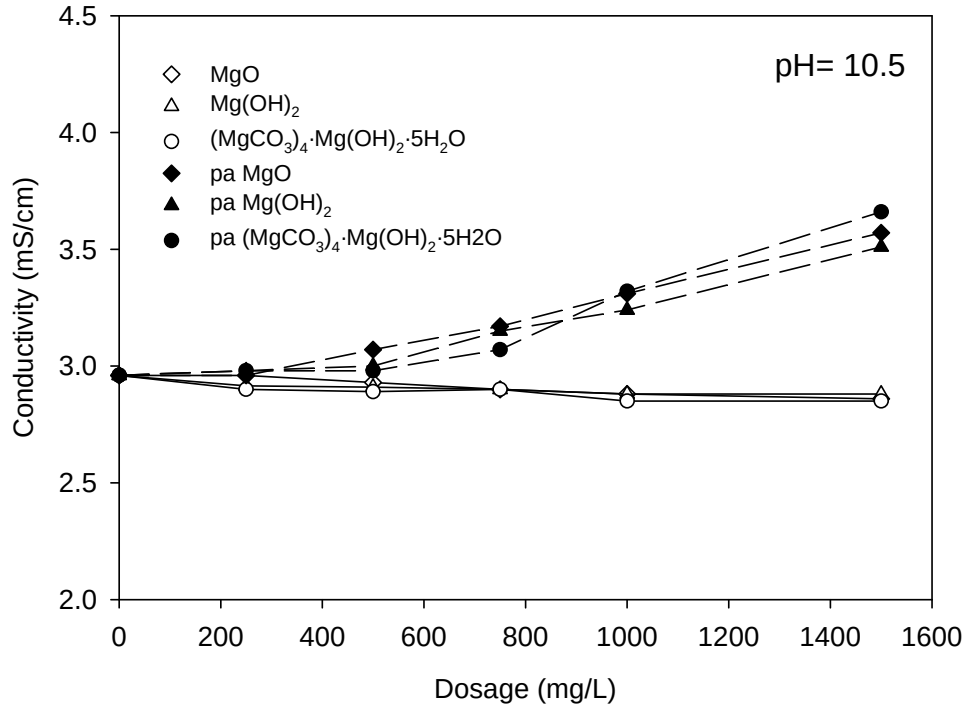
Figure 5- Final magnesium vs. dosage at different initial pH using MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ with and without pre-acidification.

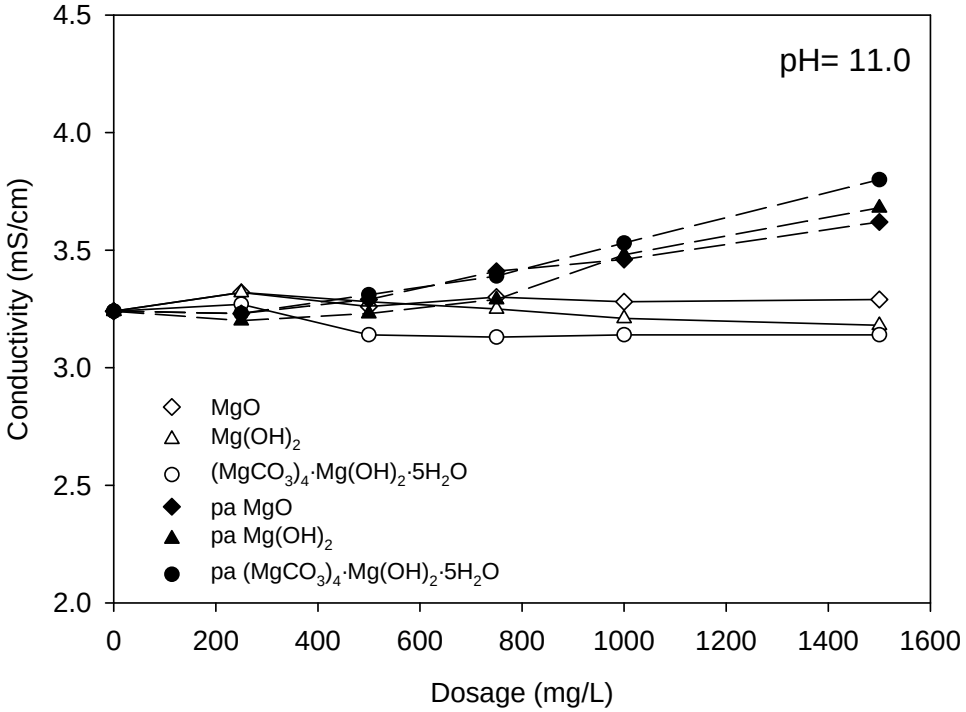
On the other hand, working at 60-80% recovery rates involves an increase in the conductivity of the RO rejects of around 2.5-5 times with respect to that of the feed water. Taking into account the discharge limit for conductivity in the effluent (7.5 mS/cm), the conductivity of the treated water should be in the range of 1.5-3.0 mS/cm to avoid the need of a reject post-treatment. Although the conductivity of the treated water was mostly increased due to pH adjustment, as shown in figure 6, the increase in conductivity with respect to blank values was higher when pre-acidified compounds were used due to the increase of dissolved magnesium and sulphates. In contrast, the increase in conductivity was lower at higher pH due to the precipitation of dissolved species such as $Mg(OH)_2$ and magnesium silicates. At pH=11.5 the increase in conductivity compared to the non pre-acidified magnesium compounds was lower than at pH=10.5. (0.1-0.2 mS/cm at pH=11.5 versus 0.6 mS/cm at pH=10.5). With 1500 mg/L of MgO, the final conductivity was 3.6 mS/cm at pH 10.5 and 11.0 and 3.9 mS/cm at pH 11.5. In the case of $Mg(OH)_2$, the final conductivity was 3.5, 3.6 and 3.8 mS/cm for pH=10.5, 11.0 and 11.5, respectively. Finally, with

$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, the highest conductivities obtained were: 3.7 mS/cm at pH=10.5, 3.8 mS/cm at pH 11.0 and 3.9 mS/cm at pH 11.5. The use of pre-acidified magnesium compounds compared to soluble ones has the important advantage of increasing less the conductivity of the waters, i. e.0.5 mS/cm in the conditions of maximum silica removal (pH=11.5 and 1500 mg/L dosage) [22]. This would imply 1.25-2.5 mS/cm lower conductivity in the RO rejects, which is a great achievement related to the RO rejects management and treatment.

Alkalinity is another important parameter to understand the silica removal mechanism during the softening process as it allows monitoring the precipitation of $Mg(OH)_2$, $CaCO_3$ and different calcium or magnesium silicates. In this case, silica removal by precipitation of calcium carbonate or calcium silicate is considered negligible compared to the removal by magnesium due to its higher efficiency on silica removal [21] and the high concentration of dissolved magnesium present in the water. pH and alkalinity varied in parallel with silica removal: the higher the silica removal, the higher the decrease in pH and alkalinity. The final pH and alkalinity were determined by two facts: the pH adjustment before the addition of the magnesium compound and the pH decrease caused by the precipitation of $Mg(OH)_2$ or the precipitation of magnesium silicates. Regardless the compound, pH decrease was greater with pre-acidification than without. When focusing on pre-acidified compounds, at pH=10.5 and 11.5, $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ was the product with the highest pH decrease and at pH=11.0, the decreases obtained with $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ were very close. pH should also be in the range 7.5 ±1.0, to avoid a pH "shock" when reusing the treated water within the process which could produce organic and inorganic deposits, especially microstickies and secondary stickies [26]. Additionally, according to the discharge limit of the paper mill studied, the RO rejects should have a pH between 6.5 and 9.5. With all the treatments, the final pH was over these limits and that would require a final pH-adjustment. Alkalinity of the treated waters increased with the initial pH of the water and decreased with the magnesium compound dosage. Alkalinity consumption was lower than 100 mg/L $CaCO_3$ with the three pH values and maximum dosage of magnesium compounds, presenting little variation as in the case of pH.

Sulphates contents was in all cases the sum of sulphates present in the original water and the sulphates added with each dose due to pre-acidification with H_2SO_4. Sulphates added to water with each dosage were 130, 250, 380, 500 and 750 mg/L at the 5 dosages tested (250-1500 mg/L), respectively.


pH= 10.5
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pa MgO
pa Mg(OH)2
pa (MgCO3)4·Mg(OH)2·5H2O
Conductivity (mS/cm)
Dosage (mg/L)
4.5
4.0
3.5
3.0
2.5
2.0
0
200
400
600
800
1000
1200
1400
1600


pH= 11.0
MgO
Mg(OH)2
(MgCO3)4·Mg(OH)2·5H2O
pa MgO
pa Mg(OH)2
pa (MgCO3)4·Mg(OH)2·5H2O
Conductivity (mS/cm)
Dosage (mg/L)
4.5
4.0
3.5
3.0
2.5
2.0
0
200
400
600
800
1000
1200
1400
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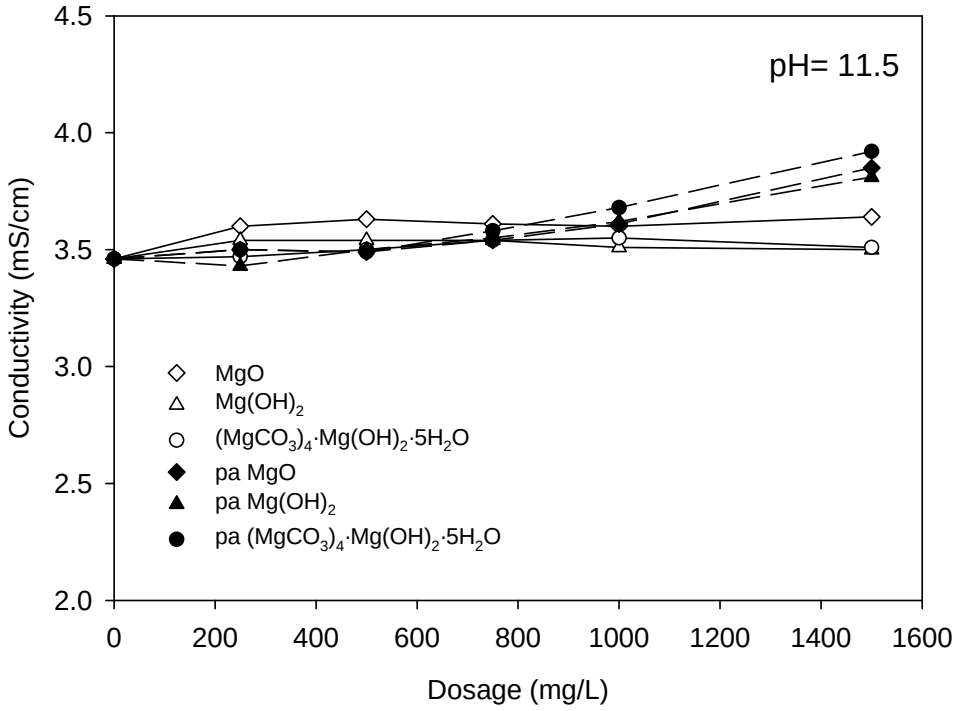

Figure 6- Final conductivity vs. dosage at different initial pH using MgO, $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ with and without pre-acidification.

Regarding COD, its removal increased with the dosage when using the pre-acidified compounds, but the variation in COD removal with the same dosage at different pH conditions was lower than 2%. The maximum COD removal efficiencies achieved with 1500 mg/L of the pre-acidified magnesium compounds were: 19% with MgO, 19% with $Mg(OH)_2$ and 16% with $(MgCO_3)_4 \cdot Mg(OH)_2$.

Turbidity showed small variations with pH and dosage. It decreased slightly with the initial pH of the water and increased with the magnesium compound dosage. The final turbidity in the clarified water varied between 90-200 NTU while dissolved turbidity in the treated water was in the range of 6-10 NTU.

3.3. Optimization of the pH regulator

As high pH is required for silica removal, the selection of the pH regulator is a key factor, both in terms of costs and treated water characteristics, such as conductivity and COD. The convenience of using lime milk as pH regulator instead of caustic soda was studied using pre-acidified MgO as magnesium source. The main advantages of lime compared to caustic soda is that it is cheaper but also, as it is a sparingly soluble compound, it produces a milder conductivity increase which, for this particular application, is very important. Another advantage is that it improves the COD removal [22]. By contrast, the use of lime milk also brings along some disadvantages such as the higher generation of sludge or the increase in the turbidity of the treated water.

First, the effect of the pH regulator on the silica removal was tested. As shown in figure 7, silica removal was increased when using lime milk. Silica removal was around 11% higher with lime milk at the lower pH values (10.5 and 11.0) and 5% at pH=11.5. With NaOH, the maximum removal rates obtained at each pH were 55% at pH 10.5, 68% at pH 11.0 and 74% at pH 11.5, using 1500 mg/L of pre-acidified MgO. On the other hand, maximum silica removal rates obtained with lime milk were 66, 78 and 82% at pH= 10.5, 11.0 and 11.5, respectively, using the highest dosage of pre-acidified MgO. This higher removal rates were probably due to the precipitation of $CaCO_3$ that, despite proven to be less effective than magnesium compounds, still contributes to silica removal in some extent, which could even be the most important effect for waters with high calcium and low magnesium hardness [15]. Another possibility is that silica was also removed through the formation of calcium or calcium-magnesium silicates.

As expected, the final conductivity of the treated waters was always significantly higher with caustic soda than with lime milk at all pH levels and MgO dosages (figure 8). With caustic soda, conductivity varied between 3.6-3.7 mS/cm at pH 10.5, 3.8-4.1 mS/cm at pH 11.0 and 4.2-4.3 mS/cm at pH=11.5. On the other hand, conductivity ranges with lime milk were: 2.2-2.3 mS/cm at pH 10.5, 2.3-2.4 mS/cm at pH 11.0 and 2.4-2.6 mS/cm at pH 11.5.

Turbidity in the clarified water did not vary significantly with the pH or MgO dosage. With NaOH, the turbidity of the clarified water was around 100 NTU, whereas the final turbidity of the water using lime was around 200 NTU, compared to 141 NTU in the

raw water. Turbidity of treated waters when using lime milk as pH regulator could reduced following different approaches such as using dissolved air flotation, increasing the settling time or with small dosages of flocculant in the settling tank. Moreover, prior to the RO the water is usually pre-treated in a membrane system such as UF. Although this last step would minimize the potential problems that may appear on the RO, this operation must be carefully optimized to select the correct flux and backwash interval.

Regarding COD, higher removal rates were obtained with lime milk than with caustic soda at all pH levels and $MgCl_2 \cdot 6H_2O$ dosages. For both pH regulators, COD removal increased by increasing the dosage of the Mg compound (figure 9). In the case of lime milk, with the maximum dosage of $MgCl_2 \cdot 6H_2O$, 25% of COD was removed at all pHs. On the other hand, with caustic soda, the maximum COD removal was 10% at pH=10.5 and 15% at both pH 11.0 and 11.5.

As it was demonstrated, despite the higher sludge generation and more accentuated turbidity increase, lime milk is preferred as pH regulator because it allowed: a greater silica removal (82% vs. 74%), greater COD removal (25% vs. 10%), and a considerably lower conductivity of the treated waters (2.4 vs. 4.6 mS/cm). Moreover, lime milk is cheaper than caustic soda.

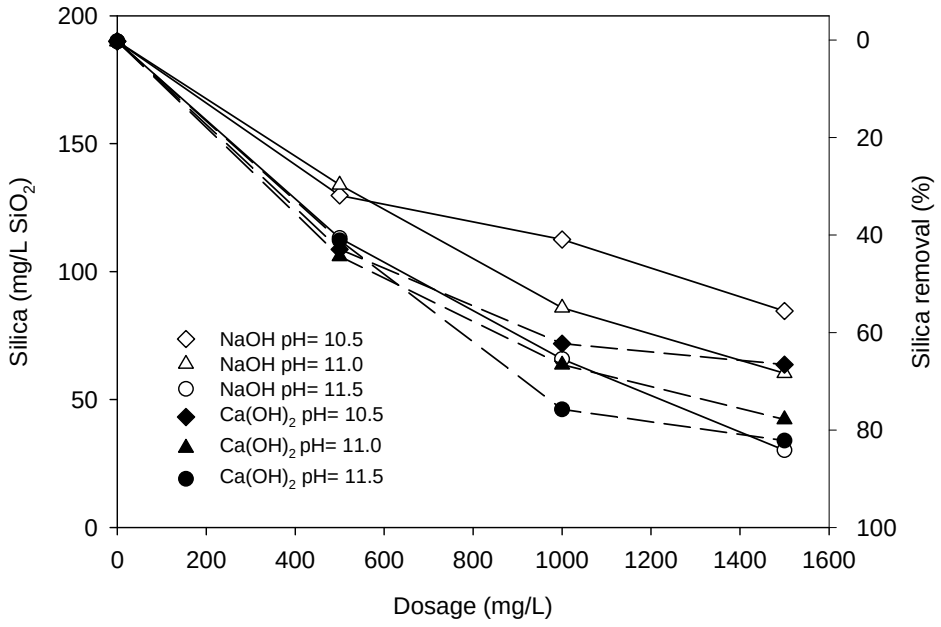

Figure 7.- Silica removal vs. pre-acidified MgO dosage at different initial pH with $Ca(OH)_2$ or NaOH as pH regulators.

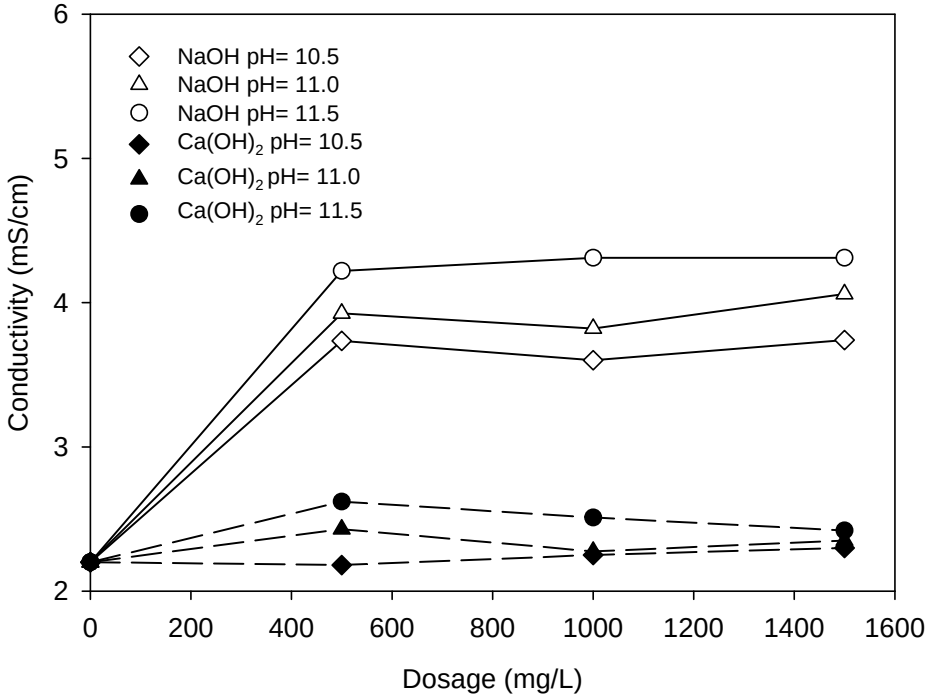

Figure 8.- Conductivity of treated waters vs. pre-acidified MgO dosage at different initial pH with $Ca(OH)_2$ or NaOH as pH regulators.

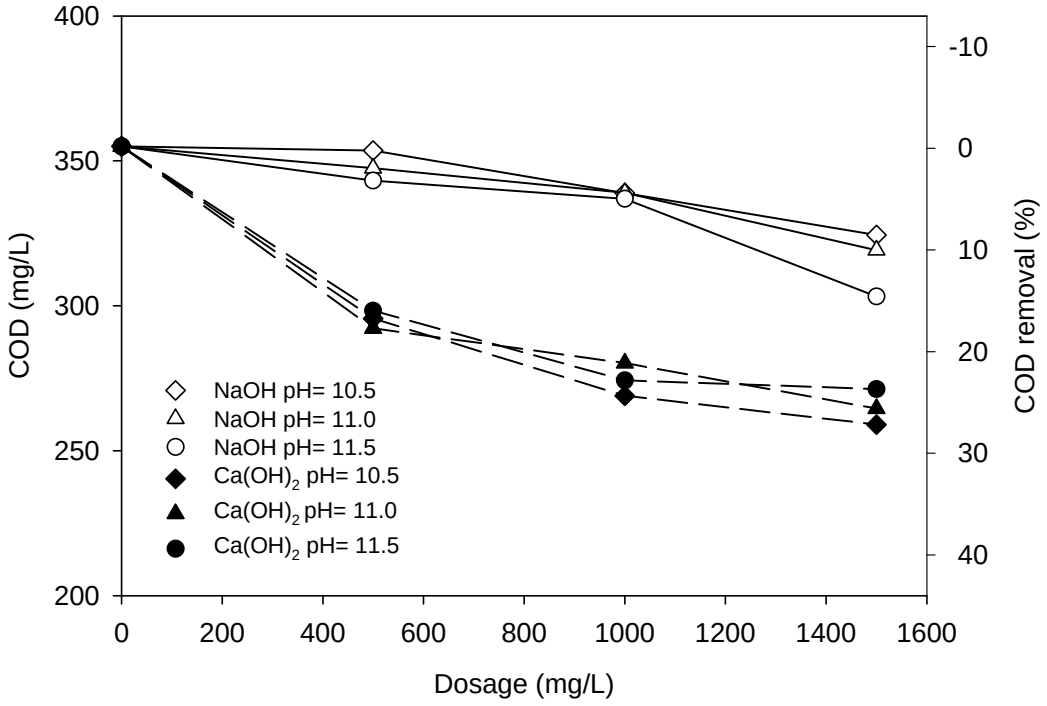

Figure 9.- COD removal vs. pre-acidified MgO dosage at different initial pH with $Ca(OH)_2$ or NaOH as pH regulators.

4.-CONCLUSIONS

Silica removal during softening is a cheap treatment to treat large volumes of water with high silica contents; however, the high operational pH required and the counter-ions of calcium and magnesium salts added are directly translated into a high conductivity of the treated water which causes operational problems in the RO and the need of a further the post-treatment of RO rejects before water discharge.

The use of sparingly soluble compounds has the advantage of adding less conductivity to water while causing no further scaling problems as they do not add counter ions to total dissolved solids. Nevertheless, silica removal obtained with these species was very limited at ambient temperature and at 15 min contact time due to the slow dissolution kinetics of these compounds. At these conditions, a maximum of 40% silica removal was obtained with 1500 mg/L of MgO at pH 11.5. With $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, removal rates lower than 20% and 10% were achieved, respectively. These low removal rates would not allow working at the high RO recoveries necessary (65-80%) without silica scaling problems, making the process not technically viable.

Pre-acidification of the magnesium compounds increased the dissolved magnesium content, and, thus, silica removal: a 86% silica removal was obtained with both MgO and $Mg(OH)_2$ and a 80% with $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$. However, previous acidification increases the conductivity of the treated waters compared to the direct use of the sparingly soluble compounds. This problem was solved by using $Ca(OH)_2$ as pH regulator instead of NaOH. In the most favourable conditions (pH 11.5 and 1500 mg/L of pre-acidified MgO), the final conductivity of the treated water was 4.3 mS/cm with caustic soda and 2.4 mS/cm with lime milk for an initial conductivity of the waters of 2.2 mS/cm. The use of lime milk as pH regulator has the additional advantage of increasing COD removal (25%) compared to 15% obtained with NaOH. As showed in the study, the use of pre-acidified MgO with $Ca(OH)_2$ as pH regulator allowed obtaining high silica removal rates with a low increase in conductivity and at low cost even at ambient temperature. These aspects make the softening an economically competitive technique compared to other silica removal techniques such as coagulation,

as the latter requires high dosages of complex hybrid coagulants to obtain similar removal rates.

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